III.B.12 Hybrid Experimental/Theoretical Approach Aimed at the Development of a Carbon-Tolerant Alloy Catalyst

Objectives

- Utilize hybrid experimental/theoretical framework, combining quantum Density Functional Theory (DFT) calculations and various state-of-the-art experimental tools, to formulate carbon-tolerant hydrocarbon reforming catalysts.
- Employ DFT calculations to develop molecular insights into the elementary chemical transformations that lead to carbon poisoning of Ni catalysts.
- Utilize DFT calculations to identify potential carbon-tolerant alloy catalysts.
- Test the alloy catalysts in steam reforming of methane, propane and isooctane.
- Characterize the tested catalysts.

Accomplishments

- We deduced molecular mechanisms that govern carbon poisoning of Ni catalysts during steam reforming of hydrocarbons.
- We identified, using DFT quantum calculation, a Sn/Ni alloy as a potential carbon-tolerant reforming catalyst.
- We tested a Sn/Ni alloy in steam reforming of methane, propane, and isooctane. We demonstrated that the alloy catalyst is carbon-tolerant under nearly stoichiometric steam-to-carbon ratios. Under these conditions, monometallic Ni catalysts are rapidly poisoned by sp2 carbon deposits.
- We utilized various characterization techniques to characterize the tested catalysts.

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Introduction

The envisioned shift to a hydrogen economy driven by rapidly evolving fuel cell technology will require an energetically feasible and environmentally friendly conversion of fossil, synthetic, and bio-renewable fuels into hydrogen. To realize this vision, major advances in catalysis are required. Improved hydrocarbon reforming, water gas shift, and preferential CO oxidation catalysts need to be formulated and synthesized. These catalysts need to perform the desired reactions with utmost efficiencies, at reduced costs, and with improved durability. Even though there is a tremendous incentive to develop more efficient catalysts, these materials are currently formulated using inefficient trial-and-error experimental approaches. In this document, we describe a novel hybrid experimental/theoretical effort aimed towards a bottom-up, knowledge-based formulation of carbon-tolerant reforming alloy catalysts.

Our objective is to utilize the hybrid experimental/theoretical framework, combining quantum DFT calculations and various state-of-the-art experimental tools, to formulate and develop carbon-tolerant hydrocarbon reforming catalysts. Unlike current state-of-the-art catalysts, which are often monometallic Ni particles adsorbed on oxide supports, oxide-supported metallic alloy catalysts are the focus of this work. These catalysts could be utilized for hydrogen production from hydrocarbons and as robust solid oxide fuel cell (SOFC) anodes for direct internal reforming.

Approach

We have employed quantum DFT calculations, catalyst synthesis, catalyst testing, and catalyst characterization to identify potential carbon-tolerant reforming alloy catalysts.

DFT calculations allow us to obtain, from first principle and with high accuracy, the ground state geometries and energies of relevant reactants, products, and transition states involved in elementary chemical reactions on catalyst surfaces. [1]

Reactor testing and various characterization techniques are applied to test the predictions of DFT calculations.

Results

One critical issue in hydrocarbon reforming is that current reforming catalysts, such as Ni, facilitate the formation of carbon structures which deactivate the catalyst. [2] The formation of carbon deposits can be partially suppressed by an introduction of steam (steam reforming). Metallic Ni is often used as a catalyst for steam reforming, and generally very high concentrations of steam are required to prevent carbon poisoning of the catalyst. [3] However, a high steam concentration is not desirable because it lowers the energy density of the products. It is imperative to design carbon-tolerant reforming catalysts that can operate with low steam concentrations.

To illustrate the problem of carbon poisoning, Figure 1a shows the results of experimental studies where the deactivation of Ni catalyst supported on YSZ during CH_4 steam reforming was investigated. It is observed that the catalyst activity decreases as a function of the time on stream. The deactivation was a consequence of the formation of large deposits of sp2 carbon networks. Transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD) experiments were utilized to identify the sp2 carbon deposits on the Ni catalyst (Figure 1b shows TEM results). Even more dramatic poisoning of Ni catalysts is observed for other hydrocarbon fuels.

We have utilized DFT calculations to calculate, from first principles, the elementary step reaction energies for methane steam reforming on Ni(111). The DFT results demonstrate that thermodynamically, the most stable state of carbon on Ni(111) is a graphene sheet adsorbed on the surface. DFT calculations also showed that carbon atoms, created in the process of hydrocarbon decomposition on Ni, can be removed from the surface by oxidation, which is accompanied by the formation of CO. The DFT studies suggest that the long-term stability of reforming catalysts is governed by their ability to selectively oxidize carbon (form C-O bonds) and remove it from the surface, while preventing the formation of C-C bonds (see Figure 2).

Motivated by these insights, we have utilized DFT to investigate the elementary steps associated with C-C and C-O bond formation on Ni. In order for C-C bonds to form on a catalyst surface, C atoms need to diffuse on the surface and collide with each other. Similarly, oxidation of carbon atoms requires collisions between C and O atoms on the surface. We have employed DFT to calculate activation barriers for C and O atom diffusion and the activation barriers for C-O and C-C bond formation. Figure 3a depicts the potential energy surface for C-O and C-C bond formation on Ni(111). We find that on Ni(111), the chemical pathways leading to C atom oxidation (C-O bond formation) have comparable overall activation barriers as those for C-C bond formation. Similar activation barriers associated with

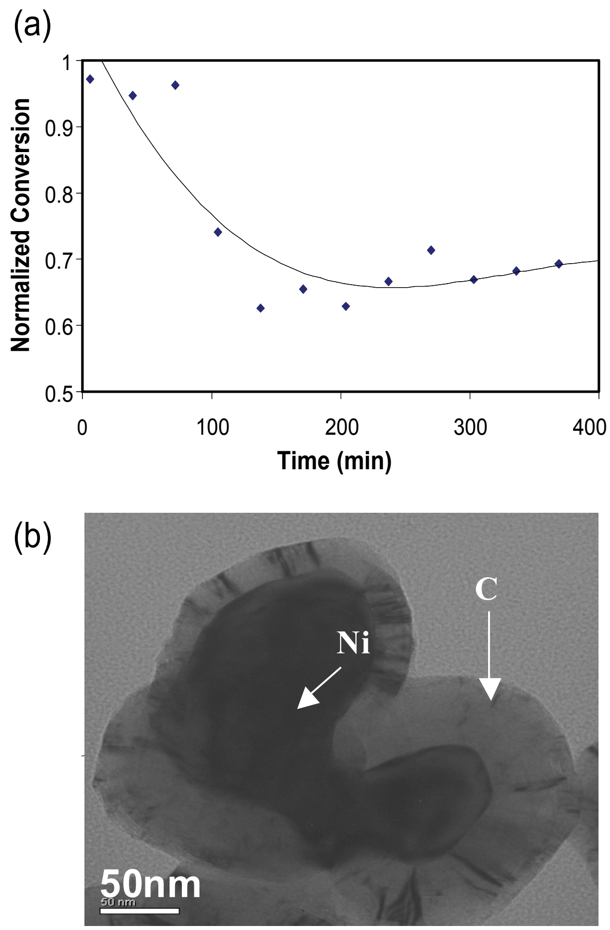

FIGURE 1. (a) Methane conversion over Ni/YSZ (Ni supported on YSZ) catalyst as a function of the time on stream. Steam to carbon ratio was 0.5. (b) TEM studies show that thick graphitic carbon deposits are formed on the Ni catalyst during methane reforming process.

Scheme 1

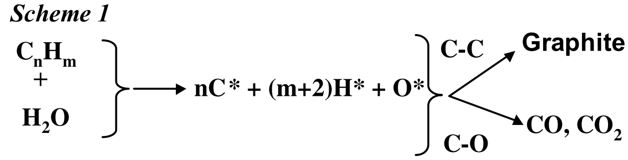

FIGURE 2. Carbon atoms can either react with each other to form sp2 carbon deposits which deactivate the catalyst, or they are oxidized to form CO which desorbs from the surface

C-O and C-C bond formation on Ni suggest that this is not an ideal reforming catalyst. Simply stated, the rate of C-C bond formation is too high to ensure the long lifetime of Ni catalysts.

The DFT calculations presented in Figure 3b show that on a Sn/Ni surface alloy, the relative kinetics of C-O and C-C bond formation is significantly different than on Ni. The dramatic Sn-induced increase in the diffusion barriers suggests that over Sn/Ni, C and O

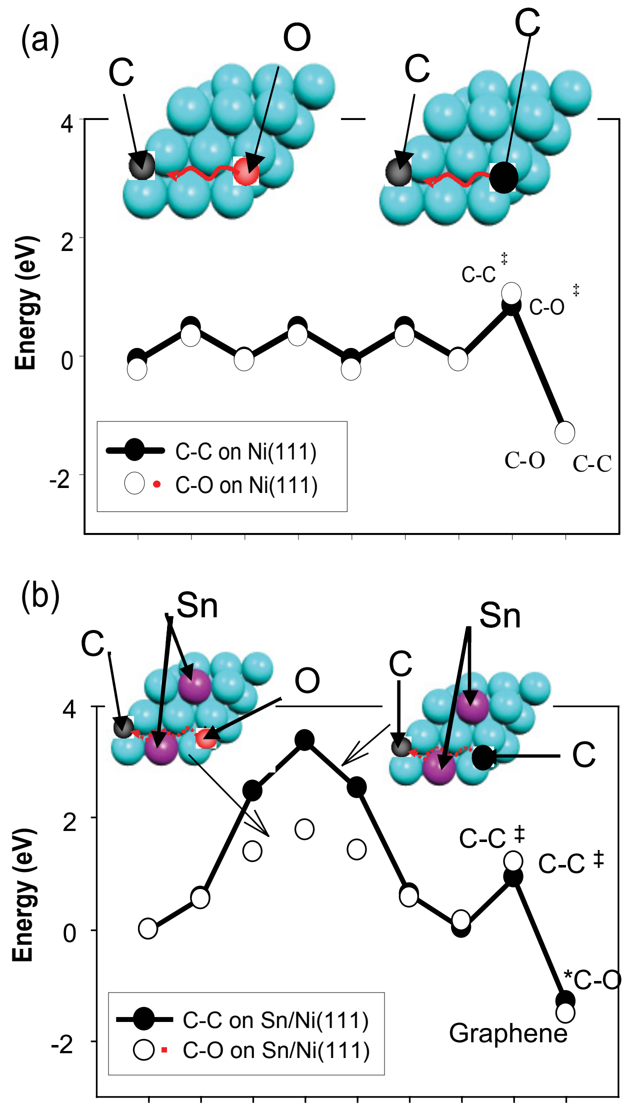

FIGURE 3. DFT calculated energies for C and O atom diffusion and C-O and C-C bond formation on a) Ni(111) and b) Sn/Ni(111). Full dark lines represent the energy landscape associated with the C-C bond formation, while red dotted lines represent the energy for C-O bond formation. Sn is represented by purple balls. C-C‡ represents the DFT calculated energy for the transition state for C-C bond formation, while C-O‡ depicts the transition state for C-O bond formation. Inserts show the lowest energy pathways for C-C (right panel) and C-O (left panel) bond formation. The pathways consists of C (dark atom, right panel) or O (red atom, left panel) atom diffusion over the surfaces and subsequent formation of C-C and C-O bonds, respectively.

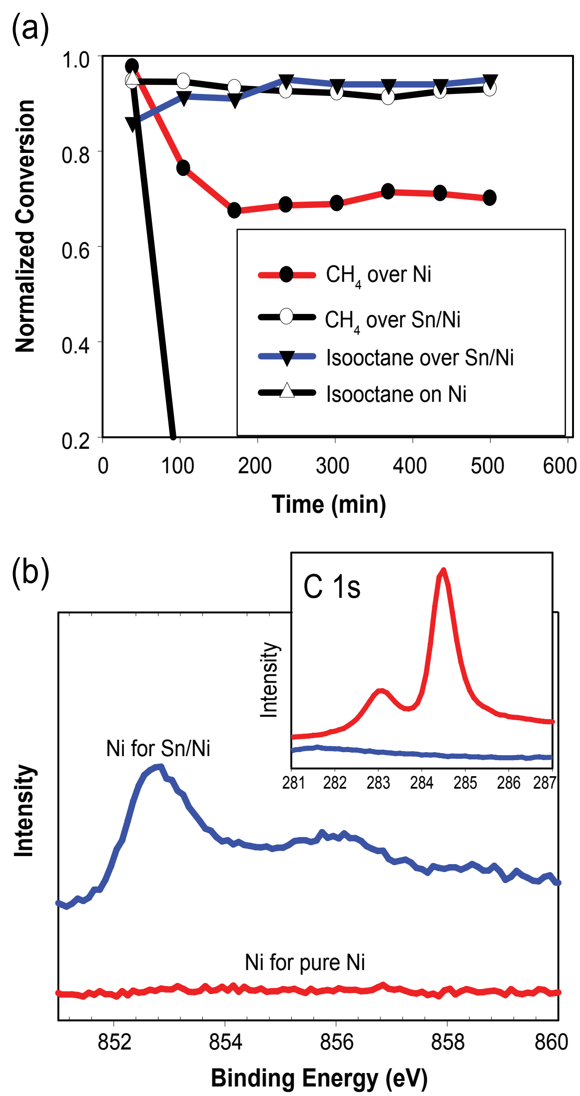

FIGURE 4. (a) Conversion by steam reforming of isooctane over a Sn/Ni alloy catalyst supported on YSZ at the steam-to-carbon ratio of 1.5. Pure Ni supported on YSZ rapidly deactivates under these conditions, while Sn/Ni is very stable. (b) XPS spectra in the energy range corresponding to the Ni signal. The Ni signal is very strong for the used Sn/Ni alloy supported on a YSZ catalyst. Conversely, the Ni signal can not be detected for monometallic Ni supported on a YSZ catalyst. The reason for this is that the Ni catalyst is covered by carbon deposits, as illustrated in the insert, where the XPS spectrum corresponding to carbon peak was collected for a pure Ni catalyst. The carbon XPS spectrum suggests that the Ni catalyst is completely covered with carbon deposits.

atom diffusion becomes kinetically limiting for the respective C-C and C-O bond formation. The DFT calculations suggest that on the alloy surface, the rate of C oxidation is much greater than the rate of C-C bond formation. Furthermore, DFT calculations show that a Sn/Ni surface alloy is the most stable phase thermodynamically, with lower formation energy than Sn bulk alloys or pure Sn and Ni phases.

The predictions of these calculations were examined in experimental studies. Pure Ni and Sn/Ni alloy catalysts were synthesized and tested in steam reforming of methane, propane, and isooctane. The results of steam reforming of methane and isooctane over Ni and Sn/Ni catalysts, obtained in our flow reactor, are shown in Figure 4a. The Sn/Ni alloy catalyst contained 1% Sn by weight with respect to Ni. Methane steam reforming was performed with a steam-to-carbon ratio of 0.5, while isooctane reforming was performed at a steam-to-carbon ratio of 1.5. Figure 4a illustrates that Sn/Ni is much more stable than monometallic Ni. For example, we observed that in isooctane steam reforming, a monometallic Ni catalyst deactivates within a few minutes. The deactivation is accompanied by a large pressure drop across the reactor, which is a consequence of a rapid buildup of carbon deposits. X-ray photoelectron spectroscopy (XPS), shown in Figure 4b, demonstrates that the Ni catalyst is completely covered by carbon deposits. In post-reaction XPS analysis of Sn/Ni, no carbon electronic fingerprint was measured, indicating that the catalyst is carbon-tolerant. Post SEM, TEM and XRD experiments also showed no signs of carbon formation on Sn/Ni, unlike the Ni catalyst which was completely poisoned by carbon deposits.

Conclusions and Future Directions

We have utilized DFT quantum calculations to develop molecular insights into the mechanism of carbon poisoning.

We have identified C-atom diffusion and C-C bond formation as two critical elementary processes that lead to the formation of extended sp2 carbon networks, which deactivate Ni catalysts. We have also determined that the long-term stability of steam reforming catalysts is governed by their capacity to selectively oxidize carbon atoms while suppressing C-C bond formation.

DFT studies demonstrated that Sn/Ni is more efficient in oxidizing and removing carbon atoms than Ni.

The reactor studies conclusively demonstrated that a Sn/Ni catalyst is much more robust than monometallic Ni for various hydrocarbons.

Post reaction SEM, TEM, EDS, XPS, and XRD characterization studies showed that the main reason for the stability of the alloy catalyst is that small amounts of Sn atomically dispersed in the Ni surface layer prevent the formation of extended sp-2 carbon networks.

Future work will involve exploring alloy catalysts as potential internal reforming anodes for SOFCs.

We also plan to explore the reforming activity of the alloys in the limit of lower loading and smaller particle size. Preliminary DFT studies indicate that the step and edge sites on our alloy catalyst should be more active for C-H bond activation.

Special Recognitions & Awards/Patents Issued

1. Best Paper Presentations, "Experimental/Theoretical Studies Aimed at the Development of Carbon-Tolerant Catalysts", Michigan Catalysis Society Annual Meeting 2006, Dow Chemicals, Midland, MI, May 2006.

2. Best Paper Competition, "Controlling Carbon Chemistry via Alloying: Hybrid Experimental/Theoretical Approach", University of Michigan Engineering Competition 2006, Ann Arbor, MI, March 2006.

FY 2006 Publications/Presentations

1. Nikolla, E., Holowinski, A., Schwank, J., Linic, S., "Controlling Carbon Surface Chemistry by Alloying: Carbon Tolerant Reforming Catalyst", Journal of the American Chemical Society, submitted 2006.

2. Nikolla, E., Schwank, J., Linic, S., "Carbon Tolerant Alloy Catalyst for H_2 Production", Journal of Catalysis, submitted 2006.

3. Nikolla, E., Linic, S., "Hybrid Experimental/Theoretical Approach Aimed at the Development of Carbon Tolerant Alloy Catalyst", ACS Colloids and Surface Science Meeting 2006, Boulder, Colorado, June 2006.

4. Nikolla, E., Linic, S., "Hybrid Experimental/Theoretical Approach Aimed at the Development of Carbon Tolerant Alloy Catalyst", NETL Contactors Meeting 2006, Pittsburgh, Pennsylvania, February 2006.

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